

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 700 104 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.03.1996 Bulletin 1996/10

(51) Int. Cl.⁶: **H01M 4/12, H01M 6/06,
H01M 4/62**

(21) Application number: **95202674.8**

(22) Date of filing: **11.06.1992**

(84) Designated Contracting States:
CH DE ES FR GB LI

(30) Priority: **11.06.1991 JP 165178/91
31.10.1991 JP 311432/91**

(62) Application number of the earlier application in
accordance with Art. 76 EPC: **92305348.2**

(71) Applicant: **Fuji Electrochemical Co., Ltd
Minato-ku, Tokyo (JP)**

(72) Inventors:
• **Shinoda, Kenichi
Toyohashi-shi, Aichi (JP)**
• **Izumi, Akihide
Kosai-shi, Sizuoka (JP)**

• **Murakoshi, Mitsuo
Hamana-gun, Sizuoka (JP)**
• **Tsutsui, Kiyohide
Sizuoka (JP)**
• **Yamashita, Katsuhiro
Toyohashi-shi, Aichi (JP)**

(74) Representative: **Charlton, Peter John
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)**

Remarks:

This application was filed on 05 - 10 - 1995 as a
divisional application to the application mentioned
under INID code 62.

(54) **Alkaline battery**

(57) A method for producing a gel form negative electrode of an alkaline battery with avoiding mercury enables uniform dispersion of zinc or zinc alloy powder and an effective metal which can be one or more of oxide or hydroxide of indium, lead, gallium, bismuth, by stirring for substantially reduced period. The method employs dry mixing of the zinc or zinc alloy powder and the effective metal in advance of mixing with a gel form alkaline electrolyte. Also, in order to obtain satisfactorily high vibration strength and impact resistance, fiber material can be added to the gel form negative electrode. The fiber material may be selected among rayon, vinylon, acryl, vinyon, polyamide, polypropylene, polyethylene, mercerized pulp, linter pulp.

EP 0 700 104 A1

Description

The present invention relates to a mercury eliminated alkaline battery. More specifically, the invention relates to an alkaline battery, which is improved in mixing ability and dispersing ability of zinc powder and effective metal in alkaline electrolyte, has high vibration strength and impact resistance, and can eliminate degradation of discharge ability under heavy load and low temperature.

In the conventional alkaline battery, a small amount of mercury is used for forming amalgam for increasing corrosion resistance by elevating hydrogen overvoltage of zinc used as primary active material for negative electrode or cathode, and for restricting passivation of zinc by converting into zinc oxide.

However, since mercury is harmful substance, there have been progressed attempts for avoiding mercury in the recent years. Among various technologies for avoiding mercury, the most advanced technology in the prior art is to add a small amount of effective metal other than mercury, such as lead, aluminum, indium, gallium, bismuth or the like to zinc for alloying. Various studies have been made with respect to influence and so forth of kind of materials to be added or adding amount for the performance of the battery, by varying compositions with variety of effective metals.

Separately from the method of alloying of zinc, there is another attempt for adhering effective metal, such as lead, aluminum, indium, gallium, bismuth or the like to zinc or zinc alloy powder. The method of adhering the effective metal to the zinc or zinc alloy has been proposed in Japanese Patent Laid-open (Kokai) Nos. 60-1775 and 60-236456. In the method proposed in the above-identified publications, the effective metal and zinc powder or zinc alloy powder are reacted for substitution in an acid solution. On the other hand, Japanese Patent Laid-open No. 1-105466 discloses a method for adhering the effective metal by directly putting oxide or hydroxide of the effective metal in a gel form alkaline electrolyte.

However, in case of the method by reaction for substitution, since the zinc or the zinc alloy powder is put in the acid solution, in which the effective metal is previously solved, and then mixed therewith by stirring, it is required substantial stirring period in order to uniformly adhere the effective metal on the surface of zinc or zinc alloy powder. Furthermore, drying process is required after stirring and mixing process, process becomes complicate.

On the other hand, in case of the method by directly putting the effective metal into the gel form electrolyte and then stirring for mixing, it also requires substantial period for uniformly distributing the effective metal relative to zinc or zinc alloy. Furthermore, by continuing stirring for long period, hydrogel structure can be destroyed to cause lowering of viscosity resulting in secondary agglomeration or precipitation of the powder.

As is well known, gel form negative electrodes are employed as the negative electrodes for the conventional alkaline battery. The gel form negative electrode is typically formed by mixing and kneading zinc powder, alkaline electrolyte and a gelling agent. The gelling agent is added for maintaining the zinc powder in uniformly distributed gel form, for increasing contacting surface area of the zinc powder and for improving reaction efficiency.

As the gelling agent, powder form gelling agent and granular gelling agent which can hold the electrolyte are typically used. The powder form gelling agent is typically carboxymethyl cellulose (CMC), poly acrylate or salts thereof. On the other hand, the granular gelling agent is typically, cross-linking and branching type poly (meta) acrylate or salts thereof as solely used or the gelling agent containing the same as primary component.

However, in case of the gel form negative electrode using the powder state gelling agent, the gel form electrolyte forming the gel form negative electrode can cause flowing in response to strong impact, such as that applied by falling down to cause destroying uniformity of distribution of zinc powder and to cause local concentration of the zinc powder. This degrades contacting condition between zinc powder particles or between zinc powder and the negative collector and thus results in lowering of performance of the battery. In the prior art, a small amount of mercury has been used for avoiding such problem. However, in the ecological viewpoint, it is highly desirable to avoid mercury.

On the other hand, in case of the granular gelling agent, the granular gelling agent swells by absorbing electrolyte and fills the gap between zinc powder particles to restrict movement of the zinc powder particles upon exertion of vibration or impact. This is effective for preventing the battery from lowering the performance due to lowering of uniformity of zinc distribution. On the other hand, even when discharging of battery is processed, the electrolyte absorbed in the granular gelling agent tends to be held therein. This creates a problem in that, degradation of heavy load discharge performance and low temperature discharge performance cannot be satisfactorily eliminated.

In order to solve the problems set forth above, various attempts, such as use of powder state gelling agent and the granular gelling agent in combination or so forth, have been made. However, no attempt has successfully achieved satisfactory improvement.

It is an object of the present invention to provide a process for forming a negative electrode of an alkaline battery which can achieve uniform mixing and distribution of a zinc or zinc alloy powder and an effective metal in a short period.

In order to accomplish the above-mentioned object, there is provided a process for forming a negative electrode comprises the steps of dry mixing one or more selected among oxide or hydroxide of indium, lead, gallium, bismuth, with zinc or zinc alloy powder to form a dry mixture, putting the dry mixture thus formed into a gelatinized alkaline electrolyte, and stirring and dispersing the mixture in the gelatinized alkaline electrolyte.

In the alternative, a process for forming a negative electrode comprises the steps of dry mixing one or more oxide or hydroxide of the above-mentioned metals, zinc or zinc alloy powder, and powder state gelling agent to form a mixture, putting the mixture into an electrolyte, and then mixing and dispersing the mixture in the electrolyte.

In case of the process, in which the effective metal and zinc or zinc alloy powder is directly mixed in the dry condition, the drying process which is required in the conventional process employing substitution reaction, can be eliminated. In addition, when the effective metal and the zinc or zinc alloy powder is put in the alkaline electrolyte in the mixed condition, the stirring period required for obtaining uniform mixing and distribution can be significantly shortened. Furthermore, by mixing the powder state gelling agent in addition, gelation of the electrolyte is progressed simultaneously with dispersing of the zinc or zinc alloy and the effective metal.

By the process for producing the negative electrode of the alkaline battery according to the present invention, the production process can be simplified in comparison with that in the conventional process. Therefore, production efficiency can be significantly improved. Also, in case that the mixture is mixed with the gelatinized alkaline electrolyte after dry mixing, stirring period required for achieving uniformly dispersed mixing can be shortened to approximately 10 minutes. This apparently contributes for improving production efficiency. Furthermore, the problem due to breakage of the gel structure will never be caused. Accordingly, the alkaline battery thus obtained has high leak-proofing ability. Therefore, the method of producing the negative electrode is suitable for avoiding mercury and uniformly adhering the effective metal on the zinc or zinc alloy powder, in the alkaline battery.

Another object of the present invention is to provide an alkaline battery incorporating the negative electrode produced through the above-mentioned process according to the present invention, which has high vibration strength and impact resistance, and can hold high performance even under heavy load and low temperature condition.

In order to accomplish the above-mentioned object, a fiber material is added to the gel form negative electrode of the alkaline battery, which gelatinized negative electrode containing alkaline electrolyte, gelling agent and zinc powder.

The preferred fiber material is alkali-proof fiber, such as rayon, vinylon, acryl, vinyon, polyamide, polypropylene, polyethylene, mercerized pulp, linter pulp or so forth.

According to the present invention, since the fiber material is added to the gel form negative electrode containing the electrolyte, the gelling agent and the zinc or zinc alloy powder, the zinc or zinc alloy powder particles are caused in the three dimensionally aggregating fiber material and maintained with restricting its motion.

Also, since the fiber material swells by absorbing the electrolyte and increasing tightness of contact between the zinc or zinc alloy powder with the negative pole collector, rising of internal resistance can be eliminated.

In addition, the electrolyte absorbed in the fiber material may be flow out by a given amount according to progress of discharging so that discharge characteristics can be stabilized.

When alkali-proof fiber, such as rayon, vinylon, acryl, vinyon, polyamide, polypropylene, polyethylene, mercerized pulp, linter pulp or so forth, is employed, the fiber may maintain its characteristics for a long period to stably provide the foregoing effect for long period.

With the alkaline battery according to the present invention, since the fiber material is added for the gel form negative electrode containing alkaline electrolyte, gelling agent and zinc or zinc alloy powder, the zinc or zinc alloy powder may be caught within the three dimensionally aggregating and maintained therein, the vibration or impact exerted on the battery can be absorbed by the fiber and motion of the zinc or zinc alloy powder particles can be restricted. This provides improvement in vibration strength and impact resistance of the negative electrode for the alkaline battery.

Other objects and advantages of the present invention will become clear from the further detailed description given herebelow in terms of the preferred embodiment of the present invention.

The present invention will be understood more fully from the detailed description given herebelow and from the accompanying drawings illustrating the preferred embodiment of the invention, which, however, should not be taken to be limitative to the invention, but are for explanation and understanding only.

In the drawings:

Fig. 1 is a graph showing relationship between stirring and mixing period and leakage rate with respect to gel form alkaline electrolyte in examples 1 and 2 of the present invention;

Fig. 2 is a graph showing relationship between stirring and mixing period and leakage rate in case that the zinc alloy powder is solved in InCl_3 solution in a comparative example 1;

Fig. 3 is a graph showing relationship between stirring and mixing period and leakage rate with respect to gel form alkaline electrolyte in a comparative example 2; and

Fig. 4 is a cross section showing construction of a cylindrical alkaline battery.

Preferred embodiments of the present invention with comparative examples will be discussed herebelow. The composition ratio of the basic materials forming the gel form negative electrode is the same for all of the embodiments and the comparative examples. It should be noted that though the following discussion will be given in terms of the gel form negative electrode with typical composition as shown in the following table, the present invention is equally applicable for any other compositions of the negative electrodes for the alkaline battery.

Also, in the shown embodiments and the comparative examples, pure indium is selected as a material of the effective metal to be added, which is known as relatively high effect in non-mercury battery. However, various metallic materials to form the effective metal are obvious to those skilled in the art. For instance, oxide or hydroxide of lead, gallium, bismuth can be solely or in combination suitable material for forming the effective metal to be added.

[EXAMPLE 1]

TABLE 1

Blended Material and Composition Ratio for Gel Form Negative Electrode	
(1) Gelling Agent (Polyacrylic Acid)	4.5 Wt parts
(2) 40 Wt% Potassium Hydroxide Electrolyte (saturated ZnO)	250 Wt parts
(3) Zinc Alloy Powder (Zn - 500 ppm Pb)	430 Wt parts
(4) Indium Oxide (In_2O_3)	0.1 Wt parts
Total	684.6 Wt parts

It should be noted that, when indium hydroxide is selected in place of the indium oxide, converting with equivalent of indium, 0.12 parts by weight of indium hydroxide will be added for 430 parts by weight of zinc alloy powder. On the other hand, an average grain size of the zinc alloy powder was approximately 150 μm , an average grain size of indium oxide was approximately 5 μm , and the average grain size of the gelling agent in a form of a dry powder was 10 μm .

PRODUCTION OF GEL FORM NEGATIVE ELECTRODE

Among the components listed above, polyacrylic acid (1) and potassium hydroxide electrolyte (2) were preliminarily mixed to prepare gel form alkaline electrolyte. Also, the zinc alloy powder (3) and indium oxide (4) were mixed by dry mixing to form a dry mixture. Mixing was performed by using ribbon blender with preventing variation of grain size. Stirring and mixing period was approximately 60 sec. Next, the dry mixture of the zinc alloy powder (3) and the indium oxide (4) is put in the gel form alkaline electrolyte. Then, stirring and mixing is performed for completing the gel form negative electrode. The gel form negative electrode is applicable for various types of batteries, such as cylindrical battery, button type battery or so forth. It should be noted that, since the zinc alloy powder and the indium oxide are mixed in the dry condition, the mixture will not be affected even when it is left for a long period. Therefore, the order of process is not necessarily specified to first prepare the alkaline electrolyte and then mix the zinc alloy powder (3) and indium oxide (4).

[EXAMPLE 2]

Among the component of the above-mentioned example 1, polyacrylic acid (1), the zinc alloy powder (3) and indium oxide (4) were dry mixed for forming a dry mixture. For mixing, ribbon blender was used. Stirring and mixing was performed for approximately 60 sec. Then, the dry mixture of polyacrylic acid (1), the zinc alloy powder (3) and indium oxide (4) was put in a preliminarily prepared alkaline electrolyte. Then, stirring and mixing was performed to complete the gel form negative electrode. This gel form electrode is applicable for various types of batteries, such as a cylindrical battery, button type battery or so forth.

[LEAK-PROOF ABILITY TEST FOR EXAMPLES 1 AND 2]

By varying the stirring period for stirring and mixing in the electrolyte from 1 min. to 20 min. samples of the gel form negative electrodes were prepared. The samples were filled in LR6 type cylindrical alkaline batteries. The batteries thus produced are left under an atmosphere of 90% of relative humidity and 60 °C of temperature. After 40 days, leakage occurring rate was checked. The results of the test is shown in Fig. 1. In Fig. 1, the white dots show the leakage occurring rate of the example 1, and the black dots show the leakage occurring rate of the example 2. Number of respective samples were 100, and number of lot were 2 kinds. Variation between respective lots was also inspected.

As can be clear from the leakage occurring rate shown in Fig. 1, although certain extent of variation between lots, the leakage occurring rate for the samples, for which the stirring period was 1 through 2 min., was 0 to 10%. When the stirring period is extended to be 5 to 10 min., the leakage occurring rate can be further reduced, and becomes substantially zero at the stirring period of 10 min. In this last case, no variation between lots could be observed.

It should be noted, when stirring was performed for 20 min., the leakage occurring rate is increased. It is considered that increasing of the leakage occurring rate is caused in that the gel structure was destroyed by stirring for long period to cause lowering of viscosity of the gel form negative electrode to cause secondary agglomeration or so forth. Accordingly, the preferred stirring and mixing period is approximately 10 min.

As set forth above, the results shown in Fig. 1 shows the fact that, by preliminarily performing dry mixing, the indium oxide uniformly adheres on each particle of the zinc alloy powder, and the desired performance can be obtained by short period stirring only for dispersion in the alkaline electrolyte.

[COMPARATIVE EXAMPLE 1]

In the composition shown in the example 1, the amounts of the polyacrylic acid (1) and potassium hydroxide electrolyte (2) were set equal to each other. These two components were preliminarily mixed to form a gel form alkaline electrolyte. On the other hand, as indium, InCl_3 having equivalent of indium equal to that in the foregoing examples was used. InCl_3 was solved in a pure water to obtain acid solution. To this acid solution, the zinc alloy powder in the same amount to the foregoing examples are put. After stirring for a period of time, varied between 2 min. to 30 min., the water was evaporated in a vacuum dryer at a temperature of 60 °C for drying. The dry powder thus obtained was put in the above-mentioned gel form electrolyte, and stirred and mixed for 10 min. for completing the gel form negative electrode.

[LEAK-PROOF ABILITY TEST FOR COMPARATIVE EXAMPLE 1]

In the comparative example 1, samples of the gel form negative electrode were prepared by employing zinc alloy powder on which indium was adhered by varying stirring period in the acid solution, in which InCl_3 is already solved, from 2 min. to 30 min. The samples of the gel form negative electrode was filled in LR6 type alkaline battery. The batteries thus produced are left under an atmosphere of 90% of relative humidity and 60 °C of temperature. After 40 days, leakage occurring rate was checked. The results of the test is shown in Fig. 2. Number of respective samples were 100, and number of lot were 3 kinds. Variation between respective lots was also inspected.

As can be clear from the leakage occurring rate shown in Fig. 2, the leakage occurring rate for the samples, for which the stirring period was 2 min., was 20 to 50% and thus unacceptably high. Also at 2 min. of stirring period, substantial fluctuation between lots was observed. By expanding the stirring period, the leakage occurring rate is decreased accordingly, and the minimum rate was reached at the stirring for 30 min. However, requirement for 30 min. stirring for each lot in order to adhere indium on the zinc alloy powder implies unacceptable for industrial application in view point of production efficiency.

[COMPARATIVE EXAMPLE 2]

In the composition of the example 1, polyacrylic acid (1) and potassium hydroxide electrolyte (2) are mixed to preliminarily form the gel form alkaline electrolyte. The zinc alloy powder (3) and indium oxide (4) in the same amounts to the foregoing example 1 were simultaneously put in the prepared gel form alkaline electrolyte. Then, by stirring and mixing, the gel form negative electrode was completed.

[LEAK-PROOF ABILITY TEST FOR COMPARATIVE EXAMPLE 2]

In the comparative example 1, samples of the gel form negative electrode were prepared by varying stirring period in the electrolyte from 2 min. to 30 min. The samples of the gel form negative electrode was filled in LR6 type alkaline battery. The batteries thus produced are left under an atmosphere of 90% of relative humidity and 60 °C of temperature. After 40 days, leakage occurring rate was checked. The results of the test is shown in Fig. 3. Number of respective samples were 100, and number of lot were 2 or 3 kinds. Variation between respective lots was also inspected.

As can be clear from the leakage occurring rate shown in Fig. 3, the leakage occurring rate for the samples, for which the stirring period was 2 min., was 20 to 50% and thus unacceptably high. Also at 2 min. of stirring period, substantial fluctuation between lots was observed. When the stirring period is in a range of 5 to 10 min. the leakage occurring rate is decreased accordingly, and the minimum rate, e.g. approximately 5% was reached at the stirring for 10 min. However, when the stirring period is further extended in a range of 20 to 30 min, the leakage occurring rate is increased. Also, fluctuation between lots becomes greater. It is considered that increasing of the leakage occurring rate is caused in that the gel structure was destroyed by stirring for long period to cause lowering of viscosity of the gel form negative electrode to cause secondary agglomeration or so forth. Therefore, the leak occurring rate cannot be satisfactorily lowered.

As can be appreciated from the discussion hereabove, with the foregoing examples 1 and 2. the effective metal as a replacement of mercury, can be uniformly adhered on each of individual zinc or zinc alloy powder particles in a short stirring period.

Fig. 4 shows a cross section of a cylindrical alkaline battery. As seen, the shown construction of the cylindrical alkaline battery includes a cylindrical positive pole can 1. A positive pole composition 2 composed of manganese dioxide and graphite, a separator 3 and a gel form negative electrode 4 are arranged in the positive pole can 1 in order in coaxial arrangement.

A negative pole terminal plate 6 is arranged in an opening portion of the positive pole can 1 via an electrically insulative seal gasket 5. The edge portion of the positive pole can 1 is clamped inwardly so that the outer circumference of the seal gasket 5 is clamped between the clamped edge of the opening portion and the outer circumferential portion of the negative pole terminal plate 6 in leak-proofing fashion. The seal gasket 5 includes a central boss portion 5a, an outer circumferential portion 5b and a connecting portion 5c interpositioned between the central boss portion and the outer circumferential portion.

On the inner center portion of the negative pole terminal plate, a negative pole collector 7 is fixed by spot welding. The negative pole collector 7 extends through a center opening defined through the central boss portion 5a of the seal gasket 5. Furthermore, for the central boss section 5a, a seal cap 8 is fitted from the inside of the battery.

When mercury is avoided from the negative electrode 4, the conventionally known brass or other pure metal can be employed as the negative pole collector 7. Preferably, plating of solder, tin, indium or so forth is provided on the surface of the metal collector so as to further restrict generation of hydrogen from the zinc powder or zinc alloy powder.

As the seal cap 8 for the alkaline battery, in which mercury is avoided from the gel form negative electrode 4, if the conventional seal cap which is formed by punch forming from a tin plated steel plate, the flush formed through punching process and exposing the elemental iron may promote generation of the hydrogen gas to degrade leak-proof capability of the battery.

Accordingly, it is preferred to form the seal cap 8 of a brass for restricting generation amount of the hydrogen gas. In this case, if degree of amalgamation is relatively high, such as greater than or equal to 0.6 Wt%, dispersion of mercury may be caused along crystal interface to lower the toughness of the seal cap to easily cause crack or to make it difficult to maintain necessary seal strength. However, according to the present invention, since mercury can be completely avoided, such problem will never be caused.

Furthermore, when the amalgamation degree is restricted lower than or equal to 1.5 Wt% or mercury is completely avoided, leak-proofing ability can be improved by employing the seal cap 8 formed by a plate material which is formed by solder plating on a brass blank plate. It is considered that such effect is achieved because that the solder plating layer prevents local cell from being formed between the zinc or zinc alloy powder and the seal cap and thus eliminate generation of hydrogen.

For demonstrating performance of the brass seal cap, seal caps 8 were prepared from steel plate, brass plate and solder plated brass plate. Using these seal caps, respectively 60 LR6 type cylindrical alkaline batteries are formed with gel form electrodes having respective amalgamation degree of 1.5 Wt%, 0.15 Wt% and 0 Wt%. These batteries are stored in an atmosphere of 90% of relative humidity and 60 °C of temperature, for 20 to 100 days for checking number

of batteries causing leakage. The results are shown in the following table 2.

TABLE 2

Relationship Between Leak-Proof Ability, Material of Seal Cap and Negative Electrode Amalgamation Degree					
1. Tin Plated Steel Plate Seal Cap					
Amalgamation Degree (Wt%)	Storing Days				
	20	40	60	80	100
1.5	0	0	0	0	3
0.15	0	0	5	12	29
0	0	10	29	60	-
2. Brass Plate Seal Cap					
Amalgamation Degree (Wt%)	Storing Days				
	20	40	60	80	100
1.5	0	7	10	25	30
0.15	0	0	0	0	5
0	0	0	0	1	10
3. Solder Plated Brass Seal Cap					
Amalgamation Degree (Wt%)	Storing Days				
	20	40	60	80	100
1.5	0	0	2	10	17
0.15	0	0	0	0	2
0	0	0	0	0	2

Next, by experimentally producing LR6 type alkaline battery having the gel form negative electrode 4 similar to the conventional one and the batteries including gel form negative electrodes, to which variety of fibers were added, performance test was performed. There followings are the particulars of respective of the batteries subject to the performance test.

[PRIOR ART 1]

The gel form negative electrode was prepared by solving ZnO in 40 Wt% KOH solution in the saturated condition, adding powder state gelling agent (powder state polyacrylate) for preparing gel form alkaline electrolyte, and adding zinc powder 60 Wt% to 40 Wt% of gel form alkaline electrolyte.

[PRIOR ART 2]

The gel form negative electrode was prepared by replacing the powder state gelling agent in the prior art example 1 with a mixture of powder state polyacrylate 50 Wt% and granular polyacrylate 50 Wt%.

[SAMPLE 1]

The gel form negative electrode was prepared by adding rayon fiber 2 Wt% relative to the weight of the zinc powder in the prior art example 1.

[SAMPLE 2]

The gel form negative electrode was prepared by adding mercerized pulp 2 Wt% relative to the weight of the zinc powder in the prior art example 1.

[SAMPLE 3]

The gel form negative electrode was prepared by adding vinylon fiber 2 Wt% relative to the weight of the zinc powder in the prior art example 1.

[SAMPLE 4]

The gel form negative electrode was prepared by adding acryl fiber 2 Wt% relative to the weight of the zinc powder in the prior art example 1.

It should be noted that, in the foregoing samples 1 to 4, the fiber materials were approximately 4 mm in the length and 0.5 to 1 denier.

Using LR6 type cylindrical alkaline batteries containing the above-mentioned 6 kinds of the gel form negative electrodes, (A) vibration test and (B) discharging performance test under heavy load and low temperature were performed.

(A) Vibration Test

By setting magnitude of vibration at 1.5 mm, and varying vibration frequency for increasing from initial 10 Hz to 55 Hz in a rate of 1 Hz/min, and then decreasing to 10 Hz in the same rate, shorting current was measured and compared with an initial value.

(B) Heavy Load and Low Temperature Discharging Performance Test

At environmental temperature of 20 °C, and with a load resistance of 2Ω, an elapsed time in continuous discharge up to final voltage (E. P. V.) of 0.9V was measured and compared with an initial value. Also, at environmental temperature of -10 °C, and with a load resistance of 10Ω, the discharge period up to the final voltage, i.e. 0.9V was measured. It should be noted that the tests were performed after storing the sample batteries for 20 days under 60 °C (accelerating condition substantially corresponding to 1 year storage at normal temperature).

The following tables 3 and 4 shows the results of the tests. The results of the test (A) are shown as percentage of magnitude of shorting current with respect to the initial shorting current. The results of the test (B) are shown as percentage of the discharge period to reach the final voltage after storing with respect to the initial discharging period.

TABLE 3

Vibration Test (%)						
Sample Battery	Sample 1	Sample 2	Sample 3	Sample 4	Prior Art 1	Prior Art 2
	87	86	94	82	75	88

TABLE 4

Heavy Load and Low Temperature Discharge Performance Test (%)						
1. Heavy Load Performance Test (2Ω Continuous Discharge, EPV = 0.9V, 20 °C)						
Sample Battery	Sample 1	Sample 2	Sample 3	Sample 4	Prior Art 1	Prior Art 2
	93	89	88	96	82	85
2. Heavy Load and Low Temperature Performance Test (10Ω Continuous Discharge, EPV = 0.9V, - 10 °C)						
Sample Battery	Sample 1	Sample 2	Sample 3	Sample 4	Prior Art 1	Prior Art 2
	95	96	93	98	89	92

(A) Results of Vibration Test

All of the samples 1 to 4 exhibit better results than that of the prior art example 1, in which only powder state gelling agent was used. Particularly, the sample 3, in which vinylon fiber was added, better results was obtained than the prior

art example 2, in which the powder state gelling agent and granular gelling agent were used in combination. From this, it should be understood that addition of soft fiber material having high impact absorbing ability is particularly effective in terms of vibration strength and impact resistance.

On the other hand, in addition to this test, discharge test was performed by connecting LR20 type alkaline battery to 1Ω of load resistance. And the batteries were fell onto an iron plate from the height of 10 cm for five times. Then, terminal voltage at both ends of the load resistor was measured. This test was performed with respect to (a) no mercury is added, (b) 250 ppm of mercury is added (amalgamation degree of 1.5 Wt%, similar to those in the market) and (c) no mercury is added and vinylon fiber is added. The results were compared. In this results, in case of the battery, to which no mercury is added, the terminal voltage was abruptly dropped upon falling impact. After recovery, certain magnitude of offset relative to the initial voltage was maintained. In contrast, in case of the battery to which 2.0 Wt% of vinylon fiber was added, only a little variation of the terminal voltage was observed upon falling impact, and the voltage was instantly recovered to the initial voltage. This is substantially the equivalent performance to the presently available battery containing 250 ppm of mercury.

(B) Results of Heavy Load and Low Temperature Discharge Performance Test

With respect to either condition of heavy load condition of 20 °C, 2Ω continuous discharge and heavy load and low temperature condition of -10 °C, 10Ω continuous discharge, the samples 1 to 4 exhibited better performance beyond the prior art example 1 and equivalent to the performance of the prior art example 2. Particularly, the sample 4, in which the acryl fiber is added, demonstrated remarkable improvement of the performance.

As discussed in detail hereabove, by adding fiber to the gel form negative electrode of the cylindrical alkaline battery, equivalent vibration strength and impact resistance to those now available can be obtained even when mercury is avoided. Furthermore, degradation of heavy load and low temperature discharge performance after storing can be reduced to certainly maintain the equivalent performance to the conventional batteries containing mercury.

It should be noted that although the foregoing discussion has been concentrated for the cylindrical battery, the present invention is equally applicable for variety of configurations or structures of alkaline batteries.

Although the invention has been illustrated and described with respect to exemplary embodiment thereof, it should be understood by those skilled in the art that the foregoing and various other changes, omissions and additions may be made therein and thereto, without departing from the spirit and scope of the present invention. Therefore, the present invention should not be understood as limited to the specific embodiment set out above but to include all possible embodiments which can be embodied within a scope encompassed and equivalents thereof with respect to the feature set out in the appended claims.

Claims

1. An alkaline battery comprising a positive electrode and a gel form negative electrode avoiding mercury and containing a zinc or zinc alloy powder and a fiber material mixed with an alkaline electrolyte, said fiber material being at least one fiber material selected among rayon, vinylon, acryl, vinyon, polyamide, polypropylene, polyethylene, mercerized pulp, linter pulp.
2. An alkaline battery as set forth in claim 1, which further comprises a positive pole container member with a closure cap for sealingly closing said container member and a negative pole collector, in which said closure cap and said negative pole collector are formed of brass.
3. An alkaline battery as set forth in claim 2, wherein said closure cap and said negative pole collector are formed of solder plated brass material.
4. An alkaline battery as set forth in claim 1, wherein said gel form negative electrode is formed through the steps of: preparing a dry mixture of one or more of oxide or hydroxide of indium, lead, gallium and bismuth and a zinc or zinc alloy powder through dry mixing; putting said dry mixture into a gel form alkaline electrolyte; and mixing and dispersing the dry mixture in the gel form electrolyte.
5. An alkaline battery as set forth in claim 1, wherein said gel form negative electrode is formed through the steps of: preparing a gel form alkaline electrolyte by mixing potassium hydroxide electrolyte and polyacrylic acid; preparing a dry mixture of a zinc or zinc alloy powder and indium oxide by dry mixing; putting said dry mixture to said gel form alkaline electrolyte; and stirring said alkaline electrolyte with said dry mixture for a predetermined period of time for mixing and dispersing said dry mixture.

6. An alkaline battery as set forth in claim 1, wherein said gel form negative electrode is formed through the steps of:
preparing a dry mixture of a zinc or zinc alloy powder and indium oxide and polyacrylic acid by dry mixing;
putting said dry mixture to said potassium hydroxide electrolyte; and
stirring said potassium hydroxide electrolyte with said dry mixture for a predetermined period of time for
mixing and dispersing said dry mixture.

5

10

15

20

25

30

35

40

45

50

55

FIG. 1

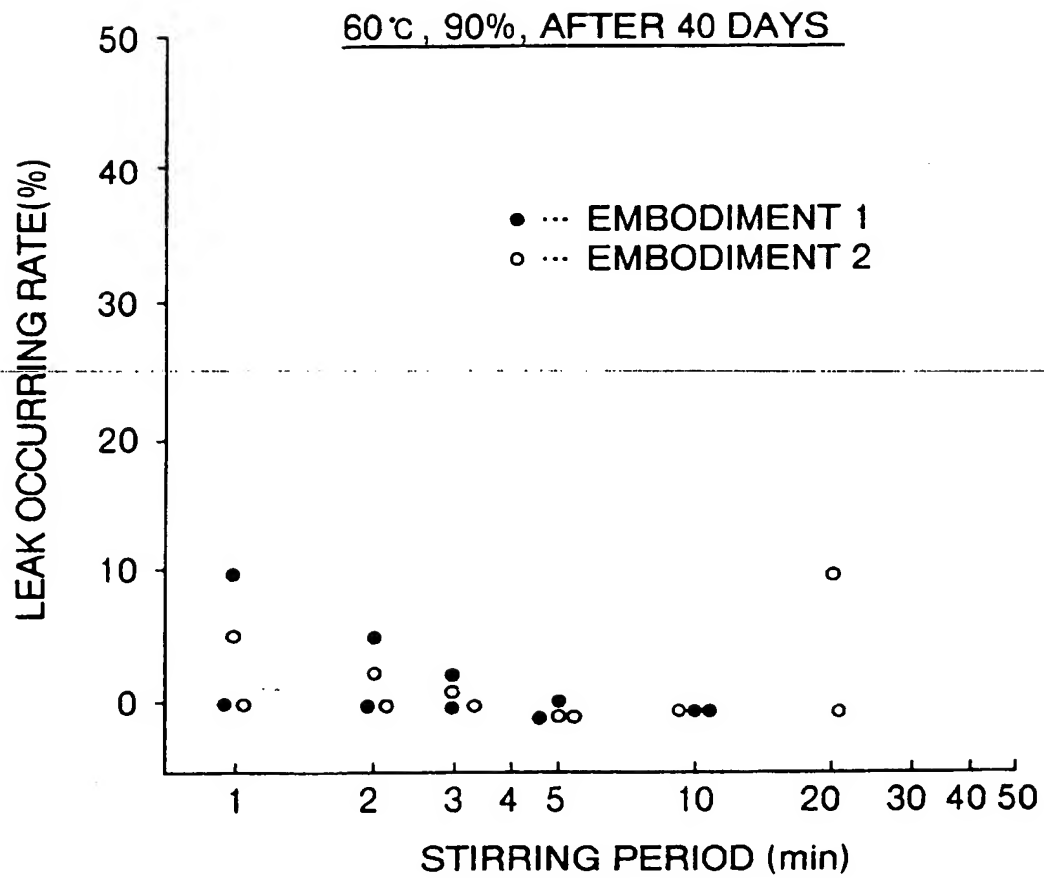


FIG. 2

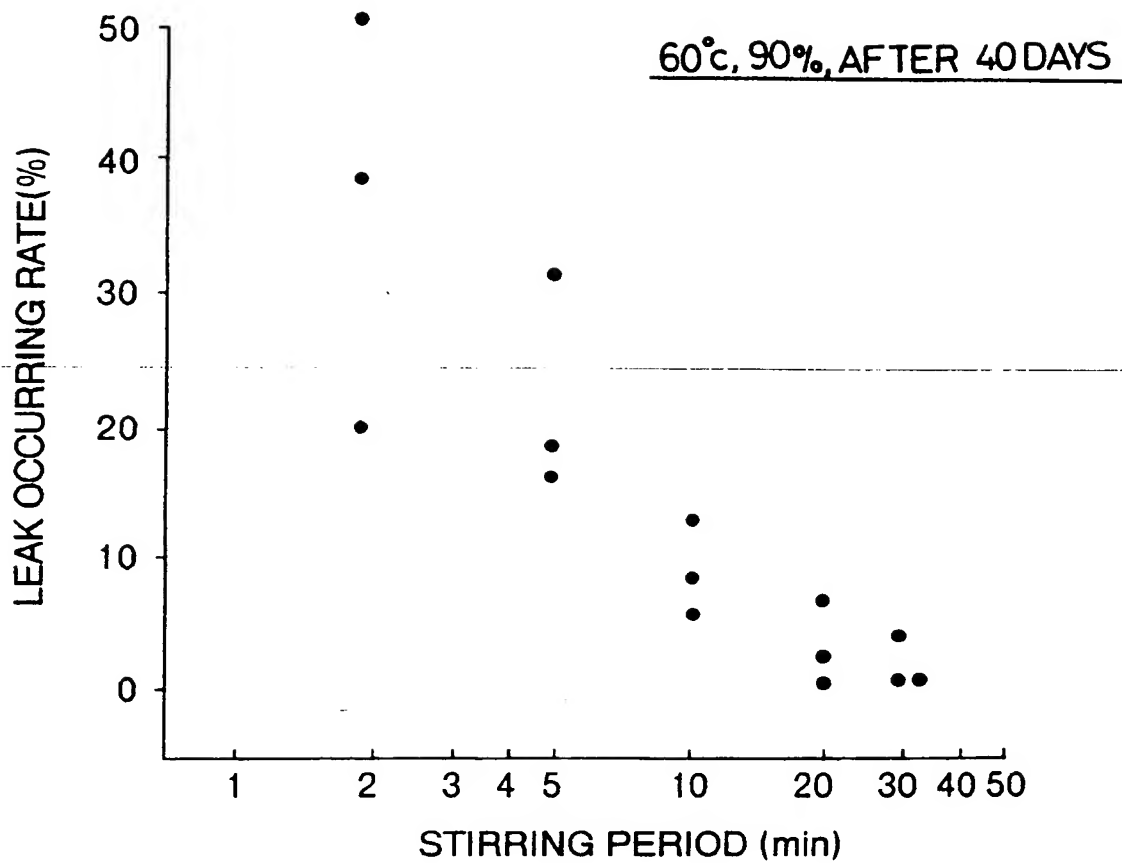


FIG. 3

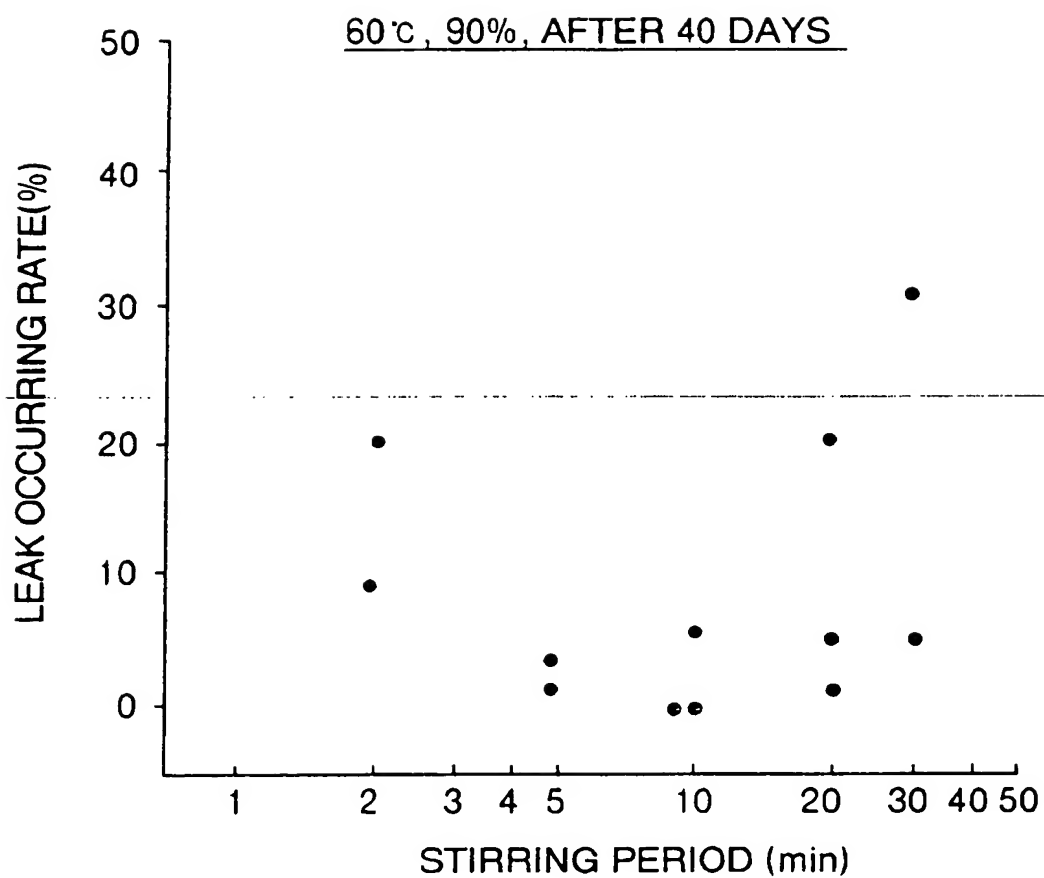
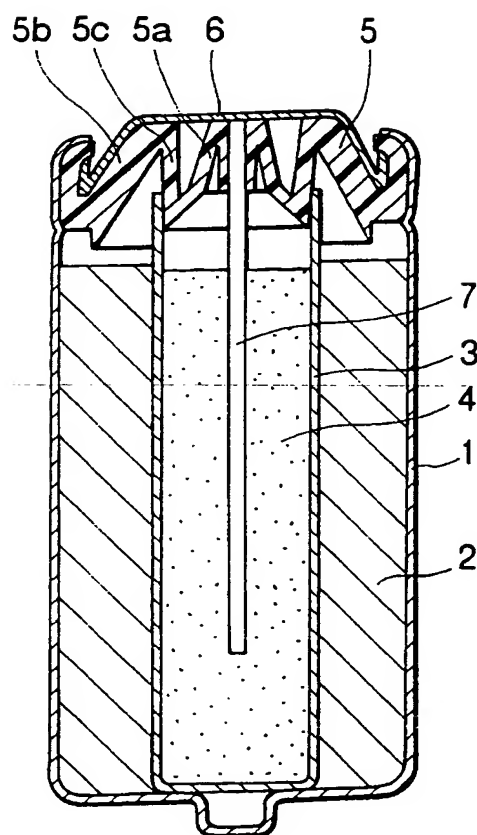


FIG. 4





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2674

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 77-31418Y & JP-A-50 096 844 (MATSUSHITA) * abstract *	1	H01M4/12 H01M6/06 H01M4/62
A	FR-A-2 634 597 (CIPEL ET WONDER) * claim 1 *	1	
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 76-00858X & JP-A-50 067 427 * abstract *	2	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 346 (E-798) 3 August 1989 & JP-A-01 105 466 (FUJI) * abstract *	4,5	
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 47 (E-299) 27 February 1985 & JP-A-59 186 256 (MATSUSHITA) * abstract *	6	<div>TECHNICAL FIELDS SEARCHED (Int.Cl.5)</div> <div>H01M</div>
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 November 1995	Examiner Andrews, M
<div>CATEGORY OF CITED DOCUMENTS</div> <div> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </div> <div> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document </div>			

EPO FORM 1503 (03.82) (P04C01)

THIS PAGE BLANK (USP 10)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)